

EXHIBIT

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TO: Professor Jim Benbrook, Chairman

COPIES: Physics Personnel Committee Members
W. K. Chu, M. Gorman, T. Hudson, J. McCauley, S. Ohnuma, G. Reiter

FROM: Paul Chu

DATE: October 6, 1992

SUBJECT: Pei Hor's Promotion and Tenure

This is a response to the request by the Physics Personnel Committee (as conveyed to me by Professor Wei-Kan Chu) to state my assessment of Dr. Pei Hor's worthiness to be promoted to Associate Professor with tenure in our Department, which has been rapidly developing in quality, breadth, and national recognition over the past few years.

I have seen Pei grow from a bright, hard-working, energetic, and conscientious graduate student in Physics to one of the most competent and successful experimental condensed matter physicists in his age-group, not just in this country but also in the world. I am extremely impressed by the quality of his work, his dedication to his work, his boldness (but with caution) in the search for novel materials and new physics, his leadership qualities and his friendliness and sincerity towards students and colleagues, based on close observations since he became a Visiting Assistant Professor of Physics in 1987 here at UH. Most important of all, he is extremely innovative and resourceful -- often able to try and to carry out sophisticated experiments by unsophisticated means. All these unusual characteristics have led to in the various breakthroughs and advances in the Experimental Solid State Physics Program, which he has been in charge of from the creation of TCSUH in 1987 until the recent reorganization of the Center. His performance and temperament as an excellent experimental condensed matter physicist and teacher, and strong evidence for his continued intellectual growth, make him one of the most (if not the most) worthy candidates in any worthy physics department in this nation. Often, the promotion to Associate Professor with tenure represents the ultimate honor that a University can bestow on a young academician. I strongly believe that, given Pei's scientific accomplishments and recognition, our Department will also be honored by promoting him to Associate Professor with tenure. I cannot think of a more worthy candidate on campus than Pei for such a promotion. I can only say that I am lucky not be competing with him for promotion at this time.

Pei joined me as a Research Assistant in our High Pressure Low Temperature Lab in the summer of 1981, after a brief (but successful) attempt to become a high energy theorist. His work on heavy fermion systems and novel materials led to a verbal offer in the summer of 1986 of a postdoctoral position at Bell Labs with Drs. Frank di Salvo and Jean Marie Tarascon. This happened at the same time I became the Program Director of the Solid State Physics Program at NSF and when the work on "light" fermion systems (oxide superconductors) started to heat up. I requested that he stay at UH and become a Visiting Assistant Professor of Physics here in the spring of 1987. His dedication to science was evident immediately when he responded to the request affirmatively, instead of going to the "heavenly" (at least in 1987) Bell Labs.

Over the last five years, Pei's contributions to our research on high temperature superconducting (HTS) and related materials have been significant and numerous. I would like

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to give only a few examples of advances that he has single-handedly made possible. He and colleagues under his direction discovered the whole series of the so-called 123 compounds $REBa_2Cu_3O_7$ -- the most important HTS compound system to date for both scientific study and large-current applications above 77 K. The results appeared in the May 1987 issue of PRL which became the most cited physics paper in 1987 (together with the article in the March 1987 issue of PRL on which Pei was also a co-author) and 1988. This paper played a crucial role in making UH among the top 10 most cited physics departments in the United States in 1987 (?) and 1988. Later, he devoted himself to the study of fluxoid motion in HTS, resulting in the discovery of a new cross-over boundary in the complex magnetic phase diagram of HTS's. Because of his knowledge of the interaction between flux lines and defects, he modified HTS's by n-irradiation and achieved a record critical current density in bulk YBCO -- the best among all existing HTS materials, be they operated at 4.2 K or higher, and particularly true in high magnetic field. Using his extensive knowledge of physics and chemistry, he recently examined all existing HTS's and proposed a new classification scheme. As a result, only a month ago he succeeded in discovering a new HTS compound with a T_c in the 30's K. I believe that his approach will lead to more exciting discoveries in the not too distant future. Aside from discovering new materials, and setting new records, he has also succeeded in unraveling a new phenomenon in C_{60} -film, *i.e.* that residual gas causes a rapid large increase in resistivity in C_{60} , especially with the aid of photons, suggesting that a new physical process occurs in the C_{60} /gas system and a possible need for the rethinking of many of the published data and, thus, of the models of fullerenes. Consequently, Pei has been asked to give invited and plenary talks at various national and international conferences. I have yet to see a young experimental physicist with a record comparable to Pei's, with the possible exception of M. K. Wu, my former student. In terms of depth and physics understanding, Pei fares better than M. K., who was only a few years ahead of Pei at UH, and who has been a Full Professor at Columbia and National Tsinghua Universities since 1989.

Pei is an excellent team worker. He worries about his own work but, at the same time, about the team. He has played a very important role in the success of TCSUH while serving both as the Associate Director for Science and as the Principle Investigator of the Experimental Solid State Physics Lab. He shows a degree of leadership and maturity seldom found in physicists of his age-group. Today's visibility of TCSUH, the Department of Physics, and the University of Houston to the outside world owes a significant debt to Pei.

Pei is not one of those who like to use outside offers as bargaining chips to promote their own positions within their own or outside universities. I found out from a colleague at UC-Riverside only later that, in 1990, they tried very hard to attract him with a faculty position equal to or above Associate Professor (it was up for negotiation) by entertaining him at Riverside royally. This would have been hard for others to refuse, but out of his intrinsic interest in physics, he asked them not to pursue the matter so that he could continue his work here. When he raises the possibility of leaving, it will be final. His departure from UH will be an irreparable loss to the Department of Physics, to TCSUH, and to the University.

Pei's promotion is not an early one since, in 1987 Prof. Weinstein, then Dean of NS&M, decided that his time of service as a Visiting Assistant Professor would be counted toward his promotion, although he is more than qualified for an early promotion.

I strongly believe that he is the best candidate in the Department for the promotion. Terry Golding is a young promising physicist who deserves consideration for early promotion. Many good things have been said by many faculty members in the Department about Terry, including

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his Army Support, which is definitely a great compliment to Terry's promise especially at this time of tight budgets. It remains a question, however, if the proposed metal/insulator (or semiconductor) superlattices for high T_c will work, since it is an old idea and has been tried by many and has failed in the past. Based on my own experience and that of others, I still remain skeptical. Of course, only time (maybe a long one, given how Nature respects theory) can tell if it eventually will work.

In summary, I highly recommend that Pei be promoted to Associate Professor of Physics with tenure on the basis of merit. He is the most worthy candidate for such a promotion in our Department of Physics. He is an excellent young physicist and teacher with few peers.



[SOLE INVENTOR]
[ORIGINAL/CIP APPLICATION]

DECLARATION AND POWER OF ATTORNEY

As a below named inventor, I hereby declare that:

(1) My residence, post office address and citizenship are as stated next to my name.

(2) I believe I am the original, first and sole inventor of the subject matter which is claimed and for which a patent is sought on the invention entitled:

SUPERCONDUCTIVITY IN SQUARE-PLANAR COMPOUND SYSTEMS

as described in U. S. Serial No. 032,041, filed March 26, 1987.

(3) I hereby state that I have reviewed and understand the contents of the above-identified specification, including the claims, as amended by any amendment referred to above.

(4) I acknowledge the duty to disclose information which is material in the examination of this application in accordance with Title 37, Code of Federal Regulations § 1.56(a).

(5) I hereby claim foreign priority benefits under Title 35, United States Code § 119 of any foreign application(s) for patent or inventor's certificate listed below and have also identified below any foreign application(s) having a filing date before that of the application(s) on which priority is claimed:

Application Number	Country	Filing Date	Priority Claim (Yes/No)
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[None]

(6) I hereby claim the benefit under Title 35 United States Code § 120 of any United States application(s) listed below and, insofar as the subject matter of each claim of this application is not disclosed in the prior United States Application in the manner provided by the first paragraph of Title 35 United States Code § 112, I acknowledge the duty to disclose material information as defined in Title 37, Code of Federal Regulations § 1.56 (a) which occurred between the filing date of the prior application(s) and the national or PCT international filing date of this application:

EXHIBIT

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<u>Application Serial No.</u>	<u>Filing Date</u>
002,089 Superconducting Composition and Method	January 12, 1987
006,991 Superconducting Compositions and Method For Enhancing Their Transition Temperatures By Pressure	January 26, 1987
012,205 High Transition Temperature Superconducting Compositions	February 6, 1987

(7) I hereby appoint the following attorney(s) and/or agent(s) to prosecute this application and to transact all business in the Patent and Trademark Office connected therewith: B.R. Pravel, Reg. No. 16,834; James B. Gambrell, Reg. No. 17,920; Lester L. Hewitt, Reg. No. 25,685; Albert B. Kimball, Jr., Reg. No. 25,689; Paul E. Krieger, Reg. No. 25,886; N. Elton Dry, Reg. No. 22,600; Charles C. Garvey, Jr., Reg. No. 27,889; Charles M. Cox, Reg. No. 30,116; Wayne E. Webb, Jr., Reg. No. 30,116; Penrose L. Albright, Reg. No. 19,082; Coke Wilson, Reg. No. 24,189; Steve Rosenblatt, Reg. No. 30,799; Keith E. Lutsch, Reg. No. 31,851; Gregory C. Smith, Reg. No. 29,441; James H. Riley II, Reg. No. 31,131; Marc L. Delflache, Reg. No. 28,942; Daniel N. Lundeen, Reg. No. 31,177; Keith M. Tackett, Reg. No. 32,008; Address all correspondence to PRAVEL, GAMBRRELL, HEWITT, KIMBALL & KRIEGER 4177 West Loop South, Suite 1010, Houston, Texas 77027; (713) 850-0909, to the attention of James B. Gambrell.

(8) I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

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Ishiguro and K. Kamimura

SUPERCONDUCTIVITY ABOVE 90 K AND BEYOND

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ABSTRACT

The discovery of high temperature superconductivity, first in 1986 at 35 K in $\text{La}_{2-x}\text{Ba}_x\text{CuO}_4$ and later in 1987 at 93 K in $\text{YBa}_2\text{Cu}_3\text{O}_7$, has been considered one of the most exciting developments in physics in the final decades of this century, with profound technological implications. In this 10th anniversary celebration, I shall begin by describing briefly two approaches adopted in the long and tortuous search for intermetallic superconductors with a higher transition temperature (T_c) that have had a significant bearing on our later work on the non-intermetallic superconductors. I shall then recall crucial steps we took in 1986, after the seminal observation made by Bednorz and Müller, which led to the exciting discovery in 1987 by the combined effort of our group in Houston and Wu's group in Huntsville. Efforts to raise the T_c over the last 10 years will be summarized, and the future prospects for T_c 's above the current record of 134 K at ambient and 164 K at high pressure will be contemplated.

1. Introduction

It has always been an exhilarating experience to be a practitioner in the field of superconductivity, where intellectual challenge and technological promise coexist. This has been especially true over the past ten years, following the discovery of high temperature superconductivity (HTSy) [1,2]. HTSy is a rapidly evolving field, where records are shattered soon after their establishment by new discoveries, and models are made obsolete shortly after their proposition by new insights. The rapid pace of progress made in the field has been unprecedented. Voluminous exciting results in all areas of HTSy science and technology have been achieved. For instance, the transition temperature (T_c) has been quadrupled, several crucial aspects of HTSy have been understood, various models have been proposed, numerous material processing techniques have been developed, and a wide variety of prototype devices have been or are being constructed and tested.

It was said by Emerson that "there is no history; there is only biography." This is especially true when the events are recounted by a person who, himself, has been heavily involved and the line between history and autobiography can become blurred. To minimize possible injustices that may be done to researchers in the field, I plan to restrict myself to one small but important area of the HTSy research, *i.e.* the search for materials with higher T_c . Some of these events has been described elsewhere [3]. In this presentation, I summarize and discuss selected events that occurred: before 1986 that sowed the seeds in our group for later HTSy-development; in 1986, that were crucial to our discovery of 93 K-HTSy soon after the discovery of the 35 K high temperature superconductor (HTSt) [1]; in 1987 when the liquid nitrogen boiling temperature of 77 K barrier was finally conquered [2]; and from 1988 to 1996, during which time advancements [4-11] were achieved continuously in raising the T_c to the current records of 134 K at ambient [9] and 164 K at

high pressures [10,11]. The prospect for higher T_c 's in the future will also be contemplated.

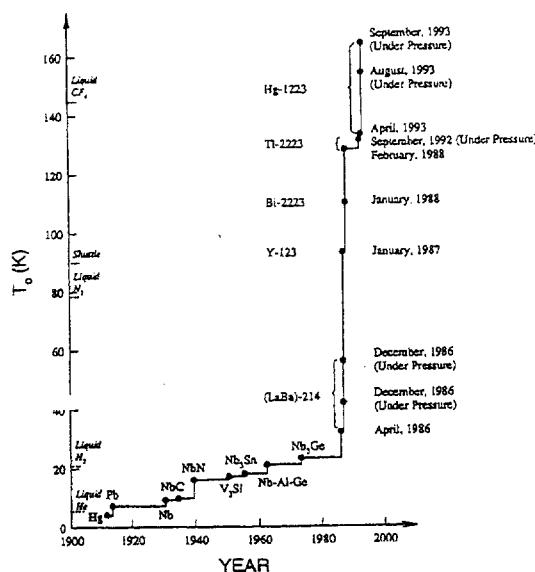


Figure 1. The evolution of T_c with time.

of the two approaches was able to lift the T_c above 23 K, studies by various groups including our own prior to 1986, give us the proper perspective on the high T_c problem, including: the possibility of a $T_c > 23$ K; the realization of the importance of optimization rather than maximization of parameters in raising T_c ; the appreciation of the significance of instabilities and dimensionality to superconductivity at higher temperatures; skills in material synthesis and characterization; and knowledge of physics and chemistry of superconductors in general and of oxides in particular.

2.1. The BCS Approach

According to the BCS theory [13], T_c is given as

$$T_c = 1.14 \Theta_D \exp[-1/N(E_F)V]$$

2. Before 1986

In spite of the enormous impact the search for novel HTSs has had on condensed matter physics research, the road to compounds with a higher T_c before 1986 was tortuous and slow, as shown in Figure 1. Until 1986, the record T_c remained at 23 K found in intermetallic Nb_3Ge films in 1972 [12], representing only a 19 K° increase since the discovery of the phenomenon in 1911. All superconductors with such a relatively high T_c then were intermetallic compounds. During this period of time, there were two general approaches adopted in the search for compounds with a T_c higher than the existing record: the BCS approach and the enlightened empirical approach. Although neither

where Θ_D is the Debye temperature, E_F is the Fermi energy, and V is the electron-atom volume.

Many experiments on various systems, based on the BCS relation [14], a higher N characteristic energy in lieu of the systems [15]. During these studies, the BCS relation is not each independent structural and/or electronic instability (structural collapse or an electron waves, etc.), before a really high instabilities and superconductivity, the incipient instabilities associated with superconductivity [16] were also avoided, including oxides near their metal

2.2. The Enlightened Empirical Approach

The most successful example of the so-called "Matthias Empirical Rule" is the ratio of valence electrons to number of a compound system usually compounds and alloys were measured. While this correlation works well for metal elements, it fails for non-metal elements, it fails for non-superconductors.

3. 1986

The work on La-Ba-Cu-O (LBCO) ushered in the era of HTSs. We were excited. We fabricated many samples and observed superconductivity immediately. It seemed to find a proper thermometer. The superconductivity researchers observed a resistance (R) drop by a factor of 2, suggesting the possibility of superconductivity above 60 K. Unfortunately, no magnetic experiment to provide such high temperatures. However,

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reached 23 K, studies by various groups made significant progress in perspective on the high T_c problem, including the appreciation of the significance of the phenomenon at higher temperatures; skills in the vledge of physics and chemistry of

where Θ_D is the Debye temperature, $N(E_F)$ the electron-density of states at the Fermi surface (E_F), and V the electron-phonon interaction. In a simplistic sense, T_c is expected to increase with an increase in one or more of the three parameters Θ_D , $N(E_F)$, and V .

Many experiments on various compounds were made and analyzed in the ensuing years, based on the BCS relation. For instance, a large V was sought in unstable compounds [14], a higher N in low-dimensional compounds [15], and a greater characteristic energy in lieu of the conventional $k\Theta_D$ in one- or two-dimensional material systems [15]. During these studies, it was realized that the three parameters in the BCS T_c -systems are not each independent of the other. Unusually large N and/or V can trigger structural and/or electronic instabilities, which in some extreme cases, give rise to a structural collapse or an electronic ordering (such as charge-density waves, spin-density waves, etc.), before a really high T_c is achieved. By examining the competition between instabilities and superconductivity using the high pressure technique, we found [14] that the incipient instabilities associated with large N and/or V are not an obstacle to higher T_c . To avoid catastrophic instabilities, novel superconducting mechanisms such as interfacial superconductivity [16] were also proposed and explored in unusual material systems, including oxides near their metal/insulator boundaries [17].

2.2. *The Enlightened Empirical Approach*

The most successful example of the enlightened empirical approach before 1986 was the so-called "Mathias Empirical Rule" proposed in 1953 [18]. The rule correlates T_c with the ratio of valence electrons to number of atoms (e/a). According to the rule, the maximum T_c of a compound system usually occurs at $e/a \sim 4.75$ and ~ 6.4 . Hundreds of intermetallic compounds and alloys were made with a T_c up to the 1972-record of 23 K in Nb_3Ge . While this correlation works well for crystalline superconductors containing transition metal elements, it fails for non-transition metal compounds and alloys, or for amorphous superconductors.

3. 1986

The work on $\text{La}-\text{Ba}-\text{Cu}-\text{O}$ (LBCO) with a $T_c \sim 35$ K in 1986 by Bednorz and Müller [1] ushered in the era of HTSs. We read their paper in early November 1986 with immense excitement. We fabricated multiphased samples of LBCO by the solid-state reaction technique that we acquired in the study of $(\text{Ba}_{1-x}\text{Pb}_x)\text{BiO}_3$ and reproduced their observation immediately. It seemed that the greatest experimental challenge at the time was to find a proper thermometer to measure in a temperature region alien to most superconductivity researchers. Even more exciting, in late November we detected a large resistance (R) drop by a factor of 80 at ~ 75 K in a multiphased sample of LBCO [19] (Fig. 2), suggesting the possibility of an even higher T_c . More R-drops were detected later above 60 K. Unfortunately, sample-aging problems prevented us from carrying out the magnetic experiment to provide more definitive evidence for a superconducting transition at such high temperatures. However, after reviewing all possible non-superconducting

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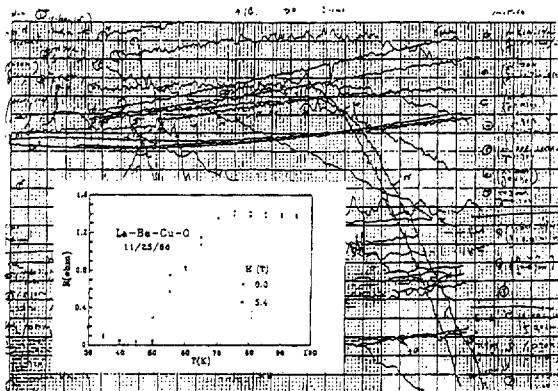


Figure 2. The $R(T)$ -curve of a multiphase LBCO sample obtained on November 25, 1986 (Ref. 3).

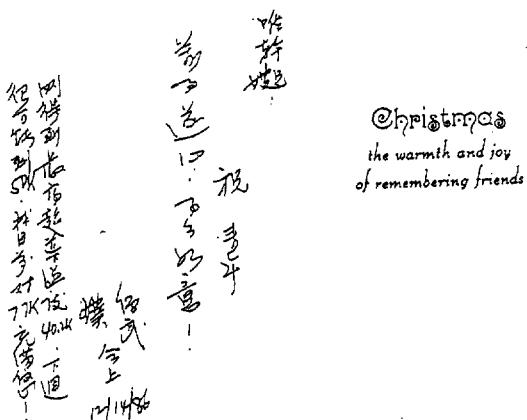


Figure 3. The Christmas card dated December 14, expressing our confidence of T_c 's above 77 K. Translation: "Just obtained highest T_c at 40.2 K, next week very likely will reach 50 K. Presently, I am full of confidence of 77 K."

transitions in various compounds, I stated that "I am now full of confidence about the 77 K (for superconductivity)," in a Christmas card to Wei-Kan Chu dated December 14, 1986 (Fig. 3).

With LBCO-samples, even though multiphased, on hand, we examined the pressure effect on their superconducting transition in an attempt to determine if the nature of the superconductivity in this compound was similar to that of the superconductivity in the low temperature superconductors (LTSrs). We found its T_c to increase at a rate almost 10 times that observed in LTSrs without a structural transition to 40.2 K at 1.3 GPa [19], a temperature previously predicted to be impossible. This observation suggested to us that the superconductivity in LBCO was different from that in LTSrs, and that T_c may not have a ceiling, a faith that played an important role in our later work.

We presented our first LBCO-results at the Materials Research Society Meeting in Boston in early December, where I invited my former student Maw-Kuen Wu then of the University of Alabama at Huntsville to join our study. Koichi Kitazawa of Tokyo told me at the Meeting that they had identified the superconducting phase responsible in LBCO to be

layered $\text{La}_{2-x}\text{Ba}_x\text{CuO}_4$ ($\text{La}-214$). Unfortunately, the frequency of samples were made more $\text{La}-214$ might exist in compounds struc that reducing the interatomic di and La by the non-magnetic Y University, a patent was drafted with the US Patent Office. By manage to raise the T_c to 42 K a

4. 1987

After destroying two of our three Pt-crucibles in an attempt to grow $\text{La}-214$ single crystals for a systematic study, we shifted our efforts to the R-drops in multiphased LBCO samples at high temperatures. While waiting for the Y, Yb and Lu we had ordered to arrive, we deliberately prepared LBCO samples with a composition distribution across them and heated them under different conditions. On January 12, 1987, a diamagnetic shift signaling the onset of superconductivity was unambiguously detected at ~ 90 K for the first time in one of the samples (Fig. 4). However, the insulating exte measurements. Since a large indicator than a R-drop, there had finally been observed. The 12, 1987 (Fig. 5) did display $\text{LaBa}_2\text{Cu}_3\text{O}_7$ ($\text{La}-123$) for the was determined in early Mar disappeared the next day. The isolate the high temperature su we decided to publish the LBC superconducting phase, provi observation was made.

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layered $\text{La}_{2-x}\text{Ba}_x\text{CuO}_4$ (La-214), which consists of one (CuO_2) -layer per unit formula. Unfortunately, the frequency of detecting a R-drop above 60 K started to plummet as our samples were made more La-214 pure. This suggested that superconductivity above 60 K might exist in compounds structurally different from La-214. The pressure data implied that reducing the interatomic distance might favor a higher T_c . Replacement of Ba by Sr and La by the non-magnetic Y, Yb, and Lu was therefore contemplated. Urged by the University, a patent was drafted in the first week of January and filed on January 12, 1987 with the US Patent Office. By replacing Sr for Ba in La-214, Maw-Kuen and students did manage to raise the T_c to 42 K at ambient [19].

4. 1987

After destroying two of our three Pt-crucibles in an attempt to grow La-214 single crystals for a systematic study, we shifted our efforts to the R-drops in multiphased LBCO samples at high temperatures. While waiting for the Y, Yb and Lu we had ordered to arrive, we deliberately prepared LBCO samples with a composition distribution across them and heated them under different conditions. On January 12, 1987, a diamagnetic shift signaling the onset of superconductivity was unambiguously detected at ~90 K for the first time in one of the samples (Fig. 4).

However, the insulating exterior of the sample prevented us from doing the resistive measurements. Since a large diamagnetic signal (~ 26% at 4 K) is a more definitive indicator than a R-drop, there was no doubt in our mind that superconductivity above 77 K had finally been observed. The X-ray diffraction pattern of the sample taken on January 12, 1987 (Fig. 5) did display a structure different from La-214; but was indexed as $\text{LaBa}_2\text{Cu}_3\text{O}_7$ (La-123) for the major phase only after the structure of $\text{YBa}_2\text{Cu}_3\text{O}_7$ (Y-123) was determined in early March. Unfortunately, the diamagnetic signal in the sample was determined in early March. Unfortunately, the diamagnetic signal in the sample disappeared the next day. The only questions that remained then were how to stabilize and isolate the high temperature superconducting (HTSg) phase. After careful consideration, we decided to publish the LBCO data so that others better equipped could stabilize the 90 K superconducting phase, provided that we stated clearly the conditions under which the observation was made.

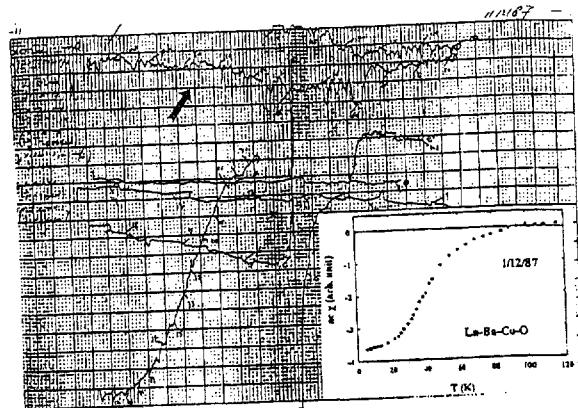


Figure 4. $\chi(T)$ for a multiphased LBCO-sample determined on January 12, 1987 (Ref. 3). Inset: Measurements after subtraction of the background.

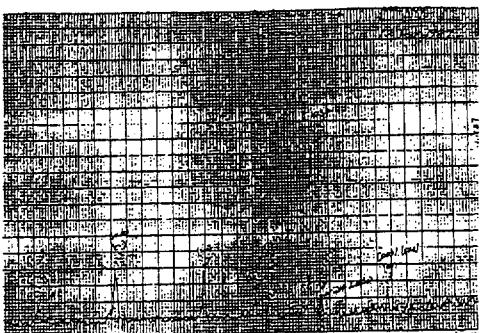


Figure 5. X-ray diffraction pattern for the LBCO-sample taken on January 12, 1987 and indexed later in March to be La-123 for the major phase (Ref. 3).

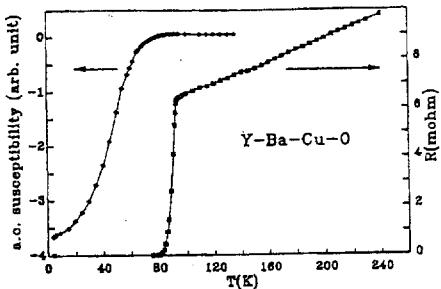


Figure 6. $R(T)$ and $\chi(T)$ for a YBCO sample measured on January 30, 1987 (Ref. 2).

The YBCO-results easily preempted my desire to write the paper on the unstable 90 K LBCO results. With the exciting YBCO results and the thought invested in the stillborn LBCO-paper, it did not take more than one evening for me to draft two papers on YBCO [2,20] which the LBCO-data was briefly included. After being reviewed by Mau-Kuen, Peiherng, and Ruling Meng, the papers were sent by express mail on February 5, 1987 to *Physical Review Letters* for publication. I was notified by Myron Strongin, editor of *Physical Review Letters*, of the acceptance of the papers on February 11.

As I started to draft a paper on these results, Mau-Kuen called on January 29, 1987 and informed my former student Peiherng Hor and me that he and his students had just observed an R-drop to zero above 77 K. We were all ecstatic. Next day, Mau-Kuen and his student Jim Ashburn flew to Houston with their sample of Y-Ba-Cu-O (YBCO) for a definitive magnetic check. As shown in Figure 6, the R-drop between 80 and 93 K observed at Huntsville was reproduced and a diamagnetic signal indicative of a superconducting transition below 91 K was detected. Using the newly arrived Y, several superconducting samples were made and tested on the same day at Houston. The long sought stable and reproducible superconductivity above the 77 K-temperature barrier was finally established. Although we did not know how to determine the structure of the superconducting phase, the X-ray pattern of the sample and the pressure effect on its T_c [20] led us to conclude that the 90 K-superconducting phase must be structurally different from the 30 K La-214 phase.

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After submitting the paper 1987 March APS Meeting held triggered by a "Dear Colleague" 1986, because our abstract on T_c was attained by pressure ar strongly felt that an exciting ph me long to convince the chairm Ashcroft, and the other council I was asked to organize the spe the University of Tokyo, Paul C Physics Institute of the Chinese AT&T Bell were invited to join order in which their respective that took place within less than on HTSy into the "Woodstock could not have dreamed that any

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After writing the paper on the unstable 90 K phase, I thought I had invested in the stillborn paper for me to draft two papers on YBCO. After being reviewed by Mau-Kuen, I sent the paper by express mail on February 5, 1987 to Myron Strongin, editor of *Journal of Superconductivity*, on February 11.

I still vividly remember the extraordinary emotion I felt when I wrote the second sentence of the paper [2], "To obtain a superconductor reaching beyond the technological and psychological temperature barrier 77 K, the liquid nitrogen boiling point, will be one of the greatest triumphs of scientific endeavor of this kind," knowing that we had achieved it. In spite of all my confidence, deep down I still felt that, no matter how remote the possibility, it might be too good to be true. There were momentary scares after the submission of the papers that my career in superconductivity could end abruptly if the 90 K superconductivity we reported were to be proven untrue. More than once, I asked my colleagues, "Can there be phenomena other than superconductivity that are able to account for our observations? Please think and think hard!" The emotional burden at the time was enormous and was relieved only after news from other labs that they had reproduced the observation [21].

The structure of the superconducting phase was soon determined to be $YBa_2Cu_3O_7$ (Y-123) in collaboration with Bob Hazen and Dave Mao at the Geophysical Lab [22]. Other labs had also cracked the structure code at about the same time [23]. It is a layered structure with the stacking sequence of $(Y)(BaO)(CuO_2)(CuO)(CuO_2)(BaO)$, with two (CuO_2) -layers separated by a (CuO) -linear chain layer per unit cell.

Once the structure was determined, we set out to determine the role of Y in 90 K HTSs by partial replacement of magnetic rare-earth for Y. We found that, even with a large fraction of Y replaced by Gd and Eu, no T_c -depression was detected, suggesting that Y is electronically isolated from the superconducting carrier system and serves mostly as a stabilizer in the compound. A whole new series of $RBa_2Cu_3O_{7-\delta}$ (R-123) with R = Y, La, Nd, Sm, Eu, Gd, Ho, Er and Lu, with a $T_c \sim 90$ K was quickly synthesized [24] in our first trial. The series was synthesized in a reduced atmosphere which we used to significantly shorten the synthesis time and thus to give us a large advantage over other groups in the early days of HTSs. Our results prompted us to propose to attain higher T_c 's by increasing the number of CuO_2 -layers per unit cell [24]. Some of the R-123 were independently discovered at about the same time by other groups [25].

After submitting the paper on R-123, I departed for the special HTSs session of the 1987 March APS Meeting held on March 16 in New York. The special session was triggered by a "Dear Colleague" rejection letter from APS in the second week of December 1986, because our abstract on LBCO was half a line over the limit. By this time, a higher T_c was attained by pressure and R-drops at temperatures above 75 K were observed. I strongly felt that an exciting physics story was on the verge of unfolding. It did not take me long to convince the chairman of the Condensed Matter Physics Council of APS, Neil Ashcroft, and the other council members to agree to add a Special Session to the Meeting. I was asked to organize the special session. Alex Müller of IBM Zürich, Shoji Tanaka of the University of Tokyo, Paul Chu of the University of Houston, Zhong-Xian Zhao of the Physics Institute of the Chinese Academy of Sciences at Beijing, and Bertram Batlogg of AT&T Bell were invited to join a panel to address their work, in the same chronological order in which their respective work on La-214 appeared in journals. The dramatic events that took place within less than two months prior to the Meeting turned the Special Session on HTSs into the "Woodstock of Physics," a moniker coined by the late Mike Schlüter. I could not have dreamed that any such event would have happened when I first proposed it.

5. 1988-96

The years between 1988 and 1996 represent a period of solid advancement and many cuprate superconductors were discovered. They may be considered to belong to or be derivable from the layered compound systems of R_2CuO_4 [R-214 (1T), with $R = La$; or R-214(1T'), with $R = Nd, Sm, Eu$ and Gd], $RBa_2Cu_3O_7$ (R-123, where $R =$ rare earths except Ce, Pr , and Tb), $Bi_2Sr_2Ca_{n-1}Cu_nO_{2n+4}$ [$Bi-22(n-1)n$, with $n = 1, 2, 3, \dots$], $Tl_2Ba_2Ca_{n-1}Cu_nO_{2n+4}$ [$Tl-22(n-1)n$, with $n = 1, 2, 3, \dots$], $HgBa_2Ca_{n-1}Cu_nO_{2n+2+\delta}$ [$Hg-12(n-1)n$, with $n = 1, 2, 3, \dots$], $CuBa_2Ca_{n-1}Cu_nO_{2n+2+\delta}$ [$Cu-12(n-1)n$, with $n = 1, 2, 3, \dots$]; and $A_{1-x}BxCuO_2$ (with $A =$ alkaline earth, $B =$ alkaline earth or vacancy), and Sr_2CuO_4 . They have also set new T_c -records and contributed to debates on the occurrence of HTSy. In this section I shall briefly comment on these systems except the first two, that have already been discussed.

5.1. $Bi-22(n-1)n$

As 1987 came to a close, T_c stagnated at 93 K. Some noted that the accumulated man-hours devoted to HTSy in 1987 probably exceeded all those devoted to low temperature superconductivity over the preceding 75 years, over-zealously concluding that $T_c > 93$ K could only be found in non-cuprate materials, if it existed at all. Their premature predictions were shattered by Maeda *et al.* who discovered [4] superconductivity above 100 K in the $Bi-Sr-Ca-Cu-O$ (BSCCO) system in January 1988.

In the summer of 1987, Michel *et al.* reported [26] an important observation of superconductivity in $Bi-Sr-Cu-O$ at ~ 8 K, which turned out to be the $n = 1$ member of the $Bi-22(n-1)n$ system. Independently, in an attempt to expand the HTSg material base, Maeda *et al.* decided to replace the trivalent rare-earth element in R-123 by elements from the V-b group in the Periodic Table, such as Bi and Sb, which are trivalent and have ionic radii similar to the rare earths. They succeeded in detecting superconductivity above 105 K in multiphase samples of BSCCO [4]. The crystal structures of three members of the homologous series $Bi-12(n-1)n$ with $n = 1, 2$, and 3 were soon determined [27], showing layered stacking sequence of $(BiO)_2(BaO)(CuO_2)(Ca)(CuO_2)(BaO)$ with n (CuO_2)-layers separated by $n-1$ (Ca)-layers, for $Bi-22(n-1)n$. The new record $T_c = 110$ K was attributed to the $n = 3$ members; and 22 and 80 K to members for $n = 1$ and 2, respectively. T_c clearly increased with n , as was predicted by us earlier [20]. Unfortunately, T_c was later shown to decrease with $n > 3$. It is interesting to note that it took Hazen *et al.* less than 48 hours to determine the $Bi-1212$ structure after receiving the samples from us. The acceleration of HTSy-research was clearly evident.

5.2. $Tl-22(n-1)n$

Following the similar rationale in forming R-123 [2,20], Sheng and Hermann started to substitute the trivalent nonmagnetic Tl for R by the end of 1987. After overcoming some problems associated with sample synthesis due to the low melting point and high volatility of Tl_2O_3 , they detected superconductivity above 90 K in a multiphased sample with a

nominal composition of $TlBa_2Ca$ by Ca, they discovered [5] (TBCCO) in February 1987. soon determined afterward to (TlO)₂-double layer [29]. T_c members, respectively. In Se enhanced to 131 K by the appli

5.3. $Hg-12(n-1)n$

As early as 1991, attempts we Cu in the (CuO)-chain layer in the $n = 1$ member of $Hg-12(n-1)n$ single-layered cuprate. It has Schilling *et al.* [9] succeeded in $1)n$ with $n = 2$ and 3. Later $1)n$ possess $T_c = 97, 127$, and $12(n-1)n$ displays the stack ($Ca)(CuO_2)(BaO)$, with n (C structure is similar to $TlBa_2Ca$ concentration in the (HgO_2)-la of the (HgO_2)-layers, unusually large T_c enhancement by pressure was achieved, pushing T_c first to ~ 154 K at ~ 16 GPa [10], and then to 164 K at ~ 30 GPa [11], setting new T_c -records (Fig. 7) in a temperature region attainable in the Space Shuttle on the side opposite to the sun or by air-conditioner technology. $Hg-12(n-1)n$ serves as an excellent system to probe the physics of HTSy due to the unusually large doping-range associated with the large void concentration in the (HgO_2)-layer for oxygen.

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nominal composition of $\text{TiBa}_2\text{Cu}_3\text{O}_x$ in November 1987 [28]. By partially replacing the Ba by Ca, they discovered [5] a $T_c \sim 120$ K in the multiphase sample of Ti-Ba-Ca-Cu-O (TBCCO) in February 1987. The structures of members of the homologous series were soon determined afterward to be rather similar to Bi-2223 but with no modulation in the $(\text{TiO})_2$ -double layer [29]. $T_c = 90, 110$, and 125 K were assigned to the n = 1, 2, and 3 members, respectively. In September 1992, the record $T_c = 125$ of Ti-2223 was further enhanced to 131 K by the application of pressure [30].

5.3. Hg-12(n-1)n

As early as 1991, attempts were made to substitute the linearly-coordinated Hg^{+2} for the Cu in the (CuO) -chain layer in R-123. Later, Putilin *et al.* [8] synthesized $\text{HgBa}_2\text{CuO}_4+\delta$. the n = 1 member of Hg-12(n-1)n , and found a $T_c = 94$ K, the highest T_c detected in a single-layered cuprate. It has been shown that T_c increases with n at least up to 3 or 4. Schilling *et al.* [9] succeeded in raising the T_c to 133 K in a multiphase sample of Hg-12(n-1)n with n = 2 and 3. Later studies demonstrated that n = 1, 2, or 3 members of Hg-12(n-1)n possess $T_c = 97, 127$, and 134 K, when optimally doped. The crystal structure of Hg-12(n-1)n displays the stacking sequence of $(\text{HgO}_\delta)(\text{BaO})(\text{CuO}_2)(\text{Ca})(\text{CuO}_2) \dots$ $(\text{Ca})(\text{CuO}_2)(\text{BaO})$, with n (CuO_2) -layers separated by n-1 (Ca) -layers. This layered structure is similar to $\text{TiBa}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_{2n+2+\delta}$, except Hg-12(n-1)n exhibits a large vacancy concentration in the (HgO_δ) -layer for oxygen to occupy. Due largely to the local structure of the (HgO_δ) -layers, unusually large T_c enhancement by pressure was achieved, pushing T_c first to ~ 154 K at ~ 16 GPa [10], and then to 164 K at ~ 30 GPa [11], setting new T_c -records (Fig. 7) in a temperature region attainable in the Space Shuttle on the side opposite to the sun or by air-conditioner technology. Hg-12(n-1)n serves as an excellent system to probe the physics of HTSs due to the unusually large doping-range associated with the large void concentration in the (HgO_δ) -layer for oxygen.

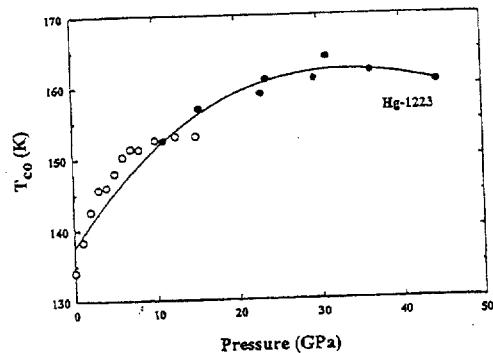


Figure 7. $T_c(P)$ for Hg-1223 . (Refs. 10,11)

5.4 $CuBa_2Ca_{n-1}Cu_nO_{2n+2+\delta}$

It has been observed that the T_c of the optimally doped homologous series $A_mX_2Ca_{n-1}Cu_nO_{2n+m+2+\delta}$, where $m = 1$ or 2 ; $X = Ba$ or Sr ; and $n = 1, 2, 3, \dots$, increases as A changes progressively from the Group VB element Bi , through the Group IIIB element Tl , to the Group IIB element Hg . It may, therefore, be possible to raise the T_c by changing A further to the Group IB element Au , Ag , or Cu . Unfortunately, our attempt to synthesize $A_mX_2Ca_{n-1}Cu_nO_{2n+m+2+\delta}$ with $A = Au$ or Ag failed due to the chemical inertness of Au and Ag . We have, therefore, tried Cu for A and discovered a 124 K superconducting phase in the system [31]. This becomes the highest T_c of cuprate without the toxic element, such as Tl or Hg .

In earlier studies, $CuBa_2Ca_{n-1}Cu_nO_{2n+2+\delta}$ with $n = 3$ and 4 was formed under high pressure with a T_c of 60 and 117 K in the $n = 3$ and 4 members, respectively [32]. $Cu_2Ba_2Cu_2Cu_3O_{9+\delta}$ was also synthesized under high pressure to show a $T_c \sim 110$ K [33]. All $Cu_mBa_2Ca_{n-1}Cu_nO_{2n+m+\delta}$ made were layered cuprates with the Cu in the (CuO_8) -layer partially replaced by C due to contamination from the high pressure graphite furnace used. The reported T_c -values are lower than the extrapolated value from T_c 's of cuprates with $A = Bi$, Tl , and Hg . By varying the synthesis conditions, such as lower pressure (~ 5.5 GPa) and temperature (~ 870 °C) than those previously reported, we succeeded [31] in synthesizing Cu-Ba-Ca-Cu-O samples with or without C-contamination with a bulk

superconducting transition up to 124 K, as shown in Figure 8. The T_c of this 124 K-phase degraded with age to ~ 80 K as the sample was kept in the desiccator for 2 months and 6 months, successively, as shown in the same Figure. These different T_c 's displayed drastically different pressure effects. The structure of the 124 K-phase has yet to be determined. However, Marezio *et al.* suggested in this Workshop [34] that the 124 K superconductivity might be associated with optimally-doped Cu-1223, although the maximum T_c of Cu-1223 achieved so far is 120 K [34].

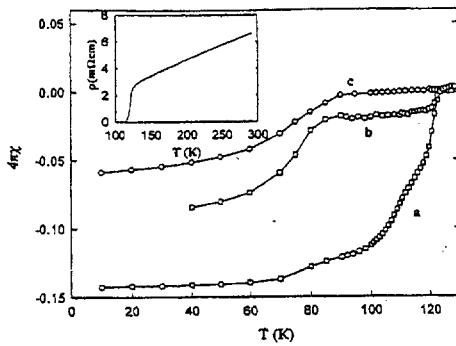


Figure 8. $\chi(T)$ and $p(T)$ for Cu-Ba-Ca-Cu-O at different ages: (a) < 3 days, (b) 2 weeks, and (c) 6 months.

5.5. R-214(1T')

In the beginning of 1989, Tokura *et al.*, discovered [6] that the charge carriers in $Nd_{2-x}Ce_xCuO_4$ with a $T_c \sim 24$ K are electron-like, in contrast to almost all others HTSs

cuprates. The compounds have to the 1T-structure of $La_{2-x}Ba$ oxygen ions to each Cu in the (1 difference between 1T and 1T'- characters in the two phases sit in the compounds. By varying and Pr), an electron-hole sym appeared to exist [35], in co Unfortunately, the highest T_c o unusual normal state properties T_c , e.g. > 90 K, are absent from distinct group of their own, m high T_c cuprates, remains unl insights to the understanding of

5.6. $A_{1-x}B_xCuO_2$

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In 1988, Siegrist *et al.* [38] member of $Ca_{n-1}Cu_nO_{2n-2}$ know not superconducting. Three y $Sr_{1-y}Nd_yCuO_2$ under 2.4 GPa Takano *et al.* [40] detected sup under 6 GPa. The nominal c excitements followed the obser doped infinite layered or the microstructure study revealed t the exact superconducting phase

Stoichiometric $SrCuO_2$ sam and found to be insulating. Thi exactly +2. Recently, an altern the defective $SrCuO_2$ to be $CuSr_2Sr_{n-1}Cu_nO_{2n+2+\delta}$ [42]. A to act as a charge reservoir to ca R-123, (HgO_8) in $Hg-12(n-1)$ propose a possible way to make through partial replacement of such as Li , Na , K , etc.

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$n = 3$ and 4 was formed under high and 4 members, respectively [32]. pressure to show a $T_c \sim 110$ K [33]. cuprates with the Cu in the (CuO_2) -layer high pressure graphite furnace used. value from T_c 's of cuprates with A = such as lower pressure (~ 5.5 GPa) reported, we succeeded [31] in T_c -contamination with a bulk

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cuprates. The compounds have a 1T' structure distinctly different from but closely related to the 1T-structure of $La_{2-x}Ba_xCuO_4$. While the 1T-phase has two neighboring apical oxygen ions to each Cu in the (CuO_2) -layer, the 1T'-phase does not. The subtle structural difference between 1T and 1T'-phases, which lead to the subtle difference in charge carrier characters in the two phases stems from the stress induced by the different ionic radii of R in the compounds. By varying the doping (*i.e.* Ce) as well as R (*i.e.* R = Gd, Eu, Sm, Nd and Pr), an electron-hole symmetry in the induction of HTSs in cuprates by doping appeared to exist [35], in consistence with some models [36] but not others [37]. Unfortunately, the highest T_c of the 1T'-phase does not exist above 30 K and many of the unusual normal state properties characteristic of the hole-doped cuprates with a very high T_c , *e.g.* > 90 K, are absent from the 1T'-compounds. Whether the 1T'-compounds form a distinct group of their own, more similar to the conventional LTSRs than the hole-doped high T_c cuprates, remains unknown. A resolution of this issue may provide critical insights to the understanding of HTSs.

5.6. $A_{1-x}B_xCuO_2$

It was pointed out earlier that T_c appeared to increase with n , the number of CuO_2 -layers per unit formula. The homologous series of layered $Ca_{n-1}Cu_nO_{2n-2}$ with large n , which form the center part of Bi-22(n-1)n or Tl-22(n-1)n had become an interesting candidate for the study for quite a while.

In 1988, Siegrist *et al.* [38] succeeded in stabilizing $(Ca_{0.85}Sr_{0.15})CuO_2$, the $n = \infty$ member of $Ca_{n-1}Cu_nO_{2n-2}$ known as the infinite layered compound. Unfortunately, it was not superconducting. Three years later, Smith *et al.* [39] synthesized electron-doped $Sr_{1-y}Nd_yCuO_2$ under 2.4 GPa and found it superconducting with a $T_c \sim 40$ K. Later, Takano *et al.* [40] detected superconductivity up to 110 K in $(Sr_{1-x}Ca_x)_{0.9}CuO_2$ prepared under 6 GPa. The nominal composition suggested hole-doped for the sample. Great excitements followed the observation, since one-model [41] seemed to suggest that hole-doped infinite layered or the 1T'-cuprate should have the highest T_c . The ensuing microstructure study revealed that the $(Sr_{1-x}Ca_x)_{0.9}CuO_2$ samples were full of defects and the exact superconducting phase is yet to be determined.

Stoichiometric $SrCuO_2$ samples were made by us recently in bulk and thin film forms and found to be insulating. This is not surprising since the Cu-valence in the compound is exactly +2. Recently, an alternative was proposed for the observed superconductivity in the defective $SrCuO_2$ to be $CuSr_2Sr_2Cu_3O_{8+8}$ or other homologous members of $CuSr_2Sr_{n-1}Cu_nO_{2n+2+8}$ [42]. A perfect structure of $SrCuO_2$ does not provide layer-block to act as a charge reservoir to carry out the so-called modulation doping such as the CuO in R-123, (HgO) in Hg-12(n-1)n, $(TlO)_2$ in Tl-22(n-1)n, or $(BiO)_2$ in Bi-22(n-1)n. We propose a possible way to make ACuO₂ superconducting and retain its structural integrity through partial replacement of the alkaline earth A by atomically small alkaline elements such as Li, Na, K, etc.

ges:

red [6] that the charge carriers in contrast to almost all others HTSs

5.7. Sr_2CuO_4

Superconductivity up to 90's K has been reported in layered Sr_2CuO_4 synthesized under high pressures [43]. Sr_2CuO_4 so prepared exhibits a similar structure to that of R-214 (1T). Unfortunately, according to the Cu-valence effect on T_c , Sr_2CuO_4 is not expected to be superconducting. Recently, oxygen vacancies were also found [44] in the CuO_2 -layers of $Sr_2CuO_{4.8}$, degrading the CuO_2 -layer integrity which has been considered to be detrimental to HTSy. Furthermore, the superconducting volume fraction in samples studied appears to be small compared with the volume-fraction of $Sr_2CuO_{4.8}$ present in these samples. A serious question concerning the identification of the reported superconductivity with the Sr_2CuO_4 phase has arisen.

We have recently succeeded in preparing samples with various volume fractions of Sr_2CuO_4 and $Sr_3Cu_2O_5$, under different conditions up to 10 GPa and 1200 °C. Some pure samples of Sr_2CuO_4 were obtained and found to be insulating and not superconducting. Superconductivity at ~ 90's K was detected in samples with the presence of the $Sr_3Cu_2O_5$. Superconducting volume fraction increases as the $Sr_3Cu_2O_{5.8}$ -content increases [45]. This demonstrates that the superconductivity at 90's K reported in the Sr_2CuO_4 is due to the impurity, such as $Sr_3Cu_2O_{5.8}$, present in the samples. Attempts to induce superconductivity in $Sr_2CuO_{4.8}$ by reduction have not yet been successful, perhaps, due to the O-defects in the CuO_2 -layer previously reported.

VI. Prospects for a Higher T_c

There appears to be a lack of consensus as to the occurrence of HTSy at such high temperatures in such an unusual class of materials, not to mention the anomalous properties of the cuprate HTSs in their normal state. The discovery of superconductors with a higher T_c 's will no doubt pose new challenges to HTSy science and make applications more practical. Thermodynamically, the higher the T_c is, the more efficient operating a HTSg device becomes. Some of the target T_c 's for applications can be determined by the coolants to be used, e.g. liquid nitrogen up to 77 K, passive cooling on the Space Shuttle in the space environment up to ~ 100 K, Freon (CF₄) up to 148 K, dry ice up to 198 K, and room temperature up to ~ 300 K. At present, there exists neither experimental nor theoretical reasons for T_c 's not to reach these target temperatures.

It is my view that a T_c above the present record of 134 K at ambient or 164 K under pressure may still be found in the layered cuprate family by increasing the number of CuO_2 -layers (n) per unit cell followed by proper doping. It has been shown that the T_c of a specific layered cuprate system increases with n up to 3 or 4 and that maximum T_c for all cuprates takes place at a carrier concentration (p) of ~ 0.16 holes per Cu-ion. The T_c drop for n > 3 or 4 has been attributed [46] to the possible depletion of p in the interior layers in a unit cell. We recently found [47] that p of cuprates with T_c > 3 or 4 indeed were underdoped with a p smaller than the optimal value of ~ 0.16 for maximum T_c to occur. Our attempt to enhance p by charging the sample with oxygen at high pressure was found to result in the decomposition of the n > 3 members of the homologous series to the n ≤ 3 ones. This may be understood in terms of the structural instability associated with large Coulomb repulsion that arises from the build up of excess charge as n increases, making doping the CuO_2 -layers and doping them uniformly in all layers increasingly difficult. The suggestion is consistent with a small but noticeable decrease of the optimal p with

increasing n [47]. We believe to developing steps to overcome the CuO_2 -layer integrity will enable Experiments are under way to test

Suggestions that cuprate is unequivocally. Therefore comp that catastrophic instabilities su charge density waves or spin possible novel mechanisms are p

Many reports of a sharp res small and always superimposed the last ten years [48]. Unfortu the existence of superconductiv the compound has to be stable (s be reproducible (from sample observations can at best be call most recent reports in 1994-95 Ca-Cu-O, Bi-Sr-Ca-Cu-O, and category. Some of them s misinterpretation of data. Howe many by reputable laboratories, tantalizing to ignore although shortening of the coherence len compounds with increasing T_c superconductivity to exist, using the very sensitive dependenc environment and thus not by a s be determined.

VII. Acknowledgement

I feel extremely blessed to be in of the most exciting development grateful to many dedicated, han Bechtold, Laurence Beauvais, I Ken Forster, Li Gao, Jason C Zhijun Huang, Allan Jacobson, Ruling Meng, Diego Ramirez, Xiong, Ya-Qi Wang and Yu-Yi mentor, the late Bernd Matthias theories. His style of doing ph work, for better or for worse superconductivity in particular therefore benefitted greatly by mundane by many traditional predictions which are treated as

n layered Sr_2CuO_4 synthesized under is a similar structure to that of R-214 effect on T_c , Sr_2CuO_4 is not expected to ere also found [44] in the CuO_2 -layers ty which has been considered to be ting volume fraction in samples studied action of $\text{Sr}_2\text{CuO}_{4.8}$ present in these cation of the reported superconductivity

uples with various volume fractions of up to 10 GPa and 1200 °C. Some pure e insulating and not superconducting. oles with the presence of the $\text{Sr}_3\text{Cu}_2\text{O}_5$ as the $\text{Sr}_3\text{Cu}_2\text{O}_{5+\delta}$ -content increases y at 90's K reported in the Sr_2CuO_4 is t in the samples. Attempts to induce ot yet been successful, perhaps, due to

he occurrence of HTSy at such high 10 to mention the anomalous properties to every of superconductors with a higher science and make applications more s, the more efficient operating a HTSg tions can be determined by the coolants ve cooling on the Space Shuttle in the up to 148 K, dry ice up to 198 K, and there exists neither experimental nor temperatures. d of 134 K at ambient or 164 K under e family by increasing the number of ping. It has been shown that the T_c of a to 3 or 4 and that maximum T_c for all f ~ 0.16 holes per Cu-ion. The T_c drop le depletion of p in the interior layers in uprates with $T_c > 3$ or 4 indeed were ie of ~ 0.16 for maximum T_c to occur. with oxygen at high pressure was found s of the homologous series to the $n \leq 3$ ictural instability associated with large f excess charge as n increases, making in all layers increasingly difficult. The able decrease of the optimal p with

increasing n [47]. We believe to properly dope cuprates with large n's to their optimal p by developing steps to overcome the doping instability described above without degrading the CuO_2 -layer integrity will enable us to achieve a T_c higher than what we have presently. Experiments are under way to test this conjecture.

Suggestions that cuprate is necessary for HTSy have been made but not yet proven unequivocally. Therefore compounds other than cuprates should not be ignored, provided that catastrophic instabilities such as structural collapse, magnetic ordering, formation of charge density waves or spin density waves, etc. are avoided. Novel materials with possible novel mechanisms are promising candidates for higher T_c 's.

Many reports of a sharp resistivity drop (but not to zero) or a diamagnetic shift (but small and always superimposed on a large paramagnetic background) have appeared over the last ten years [48]. Unfortunately, none could satisfy the four criteria I set in 1987 for the existence of superconductivity, i.e. in addition to zero resistivity and Meissner effect, the compound has to be stable (enough for definitive diagnosis) and the observation has to be reproducible (from sample to sample and from lab to lab). Therefore the reported observations can at best be called Unidentified Superconducting Objects (USO's). The most recent reports in 1994-95 of possible superconductivity above 200 K in the Hg-Ba-Ca-Cu-O, Bi-Sr-Ca-Cu-O, and Y-Ba-Cu-Se systems still belong to the same USO category. Some of them seem to be attributable to experimental artifacts or misinterpretation of data. However, the persistent sighting of USO's in multiphase oxides, many by reputable laboratories, in a similar temperature range over the last ten years, is too tantalizing to ignore although too fleeting to confirm. Could this be due to the ever shortening of the coherence length and the ever increasing of the compound stability for compounds with increasing T_c that make it more difficult to satisfy the four criteria for superconductivity to exist, using conventional diagnostic tools, or could this be caused by the very sensitive dependence of the electrical properties of many oxides on the environment and thus not by a superconducting transition? A definitive answer has yet to be determined.

VII. Acknowledgement

I feel extremely blessed to be in the right place at the right time so that I could witness one of the most exciting developments in physics and play a role in it. For that, I am forever grateful to many dedicated, hard working, and able colleagues of mine which include Jeff Bechtold, Laurence Beauvais, Daniel Campbell, Feng Chen, Wei-Kan Chu, Jeff Clayhold, Ken Forster, Li Gao, Jason Gibson, Bob Hazen, Peiheng Hor, Chao-Yuan Huang, Zhijun Huang, Allan Jacobson, Theresa Lambert, Qiu-Ming Liu, Jeff Lynn, Dave Mao, Ruling Meng, Diego Ramirez, Irina Rusakova, Chin-Sen Ting, Maw-Kuen Wu, Quan Xiong, Ya-Qi Wang and Yu-Yi Xue. Last but not least, I am also extremely thankful to my mentor, the late Bernd Matthias, who was a strict Edisonian with a deep skepticism about theories. His style of doing physics and his taste in selecting problems have influenced my work, for better or for worse, in condensed matter physics in general and superconductivity in particular. Some of my students, past and present, and I have therefore benefitted greatly by paying attention to materials which are considered to be too mundane by many traditional physicists and by not being intimidated by theoretical predictions which are treated as Sacred Writ by many experimentalists.

The work at Houston is supported in part by NSF, DoE, EPRI, the State of Texas, and the T. L. L. Temple Foundation.

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Gd 901

12 March 1987

Gd Bar Cu₃ 901

Gd	Ba	Cu
25.26	44.12	30.62

→ Gd :	200 mg	
Ba :	349.22	435.45 mg
Cu :	263.32	266.35

Mar. 27. 1987

[902] (Gd_{0.75} Ba_{0.75})₃ Cu₃ O_{6.75} 902

Gd	Ba	Cu
19.097	50.034	30.869

Gd₂O₃ : 100 mgBaCO₃ : 326.624 mg

CuO : 175.580 mg

903 Gd_{0.8} Eu_{0.2} Ba₂ Cu₃Gd₂O₃ : 100 mg

24.270

Eu₂O₃ : ~~48.544~~ mgBaCO₃ : 272.93 mg

CuO : 164.577 mg

221

H

H

158

EXHIBIT

tables

15

~~904~~

904 $Gd_{Ba_{1.8}Sr_{0.2}Cu_3}$

200 mg Gd_2O_3

391.94 mg $BaCO_3$

32.578 mg $SrCO_3$

263.35 mg CuO

905

$Gd_{Ba_1Sr_1Cu_3}$

$SrCO_3$: 162.91

Gd_2O_3 : 200 mg

$BaCO_3$: 217.8 mg

CuO : 263.3 mg

906

$Gd_{Ba_{1.2}Sr_{0.1}Cu_3}$

Gd_2O_3 : 200 mg

$BaCO_3$: 413.7 mg

$SrCO_3$: 16.289 mg

CuO : 263.35 mg

Mar. 15, 1987

Tb 1001

Tb Ba₂ Cu₃

Tb 25.459 Ba 44.003 Cu 30.537

Tb₄O₇: 100 mg

BaCO₃: 211.146 mg

CuO: 127.659 mg

READ AND UNDERSTOOD
THIS DATE BY

Tb 1001-2

Tb Ba₂ Cu_{3.2}

4th Sep 1987

Tb 1001-3

Tb Ba₂ Cu_{3.4}

Mar. 15, 1987

Nd 1101 $Nd_{2}Ba_{2}Cu_3$

Nd	Ba	Cu
23.664	45.063	31.273

Nd_2O_3 : 100 mg

$BaCO_3$: 234.588 mg

CuO : 141.834 mg

Dy 1201

Dy Ba₂Cu₃ O

Mar. 15, 1987

Dy	Ba	Cu
25.884	43.753	30.363

Dy₂O₃: 100 mg

BaCO₃: 211.626 mg

CuO : 127.947 mg

Ho 1301

Ho Ba_2Cu_3

Ho	Ba	Cu
26.170	43.584	30.246

Ho_2O_3 : 800 mg

$BaCO_3$: 208.900 mg

CuO : 126.300 mg

Mar. 15, 1987

Mar. 15, 1987

Er - 1401

Er₂Ba₂Cu₃

Er Ba Cu
26.442 43.424 30.135

Er₂O₃ : 100 mg

BaCO₃ : 206.358 mg

CuO : 1024.763 mg

~~Ti~~ ~~Ba₂Cu₃~~

Yb - 1501

~~Yb~~ ~~801~~

Yb Ba₂ Cu₃

Mar, 13, 1987

Yb	Ba	Cu
27.108	43.030	29.862

Yb₂O₃ : ~~87.8~~ 100 mg

BaCO₃ : 200.301 mg

CuO : 121.103 mg

1501
Yb - ~~Fe~~ Yb Ba-Cu₃
Yb Ba Cu
27.108 43.030 29.862
Yb₂O₃ : 100 mg
BaCO₃ : 200.301
CuO : 121.103.

Mar. 16, 87

1601

 PrBa_2Cu_3

Pr	Ba	Cu
23.24	45.31	31.45

Pr_6O_{11}	300 mg
BaCO_3	695.57
CuO	368.49

1602 $\text{Pr}(\text{Ba}_{1-x}\text{K}_x)_2\text{Cu}_3$ $x=0.1$

Pr_6O_{11} :	170.240
BaCO_3 :	$177.605 \times 2 = 355.21$
$\text{K}_2\text{CO}_3 + 1/2 \text{H}_2\text{O}$:	$81.61 \times 2 = 163.23$
CuO :	238.635

1603 $\text{Pr}(\text{Ba}_{1-x}\text{K}_x)_2\text{Cu}_3\text{O}$ $x=0.4$

Pr_6O_{11} :	170.240
BaCO_3 :	236.807
$\text{K}_2\text{CO}_3 + 1/2 \text{H}_2\text{O}$:	66.088
CuO :	238.635

1604 $\text{Pr}(\text{Ba}_{1-x}\text{K}_x)_2\text{Cu}_3\text{O}$ $x=0.6$

Pr_6O_{11} :	170.240
BaCO_3 :	157.871
$\text{K}_2\text{CO}_3 + 1/2 \text{H}_2\text{O}$:	$198.275/2 = 99.137$
CuO :	238.635

1605 $\text{PrBa}_2\text{Cu}_3\text{O}$

May 13, 1988

 Pr_2O_3 BaO CuO

1701 Cr Ba₂ Cu₃

Ex Ba Cu
10.05 53.10 36.85

Superconductivity at 93 K in a New Mixed-Phase Y-Ba-Cu-O Compound System at Ambient Pressure

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A stable and reproducible superconductivity transition between 80 and 93 K has been unambiguously observed both resistively and magnetically in a new Y-Ba-Cu-O compound system at ambient pressure. An estimated upper critical field $H_{c2}(0)$ between 80 and 180 T was obtained.

PACS numbers: 74.70.Ya

The search for high-temperature superconductivity and novel superconducting mechanisms is one of the most challenging tasks of condensed-matter physicists and material scientists. To obtain a superconducting state reaching beyond the technological and psychological temperature barrier of 77 K, the liquid-nitrogen boiling point, will be one of the greatest triumphs of scientific endeavor of this kind. According to our studies,¹ we would like to point out the possible attainment of a superconducting state with an onset temperature higher than 100 K, at ambient pressure, in compound systems generically represented by $(L_{1-x}M_x)_aA_bD_y$. In this Letter, detailed results are presented on a specific new chemical compound system with $L=Y$, $M=Ba$, $A=Cu$, $D=O$, $x=0.4$, $a=2$, $b=1$, and $y \leq 4$ with a stable superconducting transition between 80 and 93 K. For the first time, a "zero-resistance" state ($\rho < 3 \times 10^{-8} \Omega \cdot cm$, an upper limit only determined by the sensitivity of the apparatus) is achieved and maintained at ambient pressure in a simple liquid-nitrogen Dewar.

In spite of the great efforts of the past 75 years since the discovery of superconductivity, the superconducting transition temperature T_c has remained until 1986 below 23.2 K, the T_c of Nb_3Ge first discovered² in 1973. In the face of this gross failure to raise the T_c , nonconventional approaches³ taking advantage of possible strong nonconventional superconducting mechanisms⁴ have been proposed and tried. In September 1986, the situation changed drastically when Bednorz and Müller⁵ reported the possible existence of percolative superconductivity in $(La_{1-x}Ba_x)Cu_{3-\delta}$ with $x=0.2$ and 0.15 in the 30-K range. Subsequent magnetic studies⁶⁻⁸ confirmed that high-temperature superconductivity indeed exists in this system. Takagi *et al.*⁹ further attributed the observed superconductivity in the La-Ba-Cu-O system to the K_2NiF_4 phase. By the replacement of Ba with Sr,^{8,10,11} it is found that the La-Sr-Cu-O system of the K_2NiF_4 structure, in general, exhibits a higher T_c and a

sharper transition. A transition width¹⁰ of 2 K and an onset¹¹ T_c of 48.6 K were obtained at ambient pressure.

Pressure^{8,12} was found to enhance the T_c of the La-Ba-Cu-O system at a rate of greater than $10^{-3} \text{ K bar}^{-1}$ and to raise the onset T_c to 57 K, with a "zero-resistance" state¹³ reached at 40 K, the highest in any known superconductor until now. Pressure reduces the lattice parameter and enhances the Cu^{+3}/Cu^{+2} ratio in the compounds. This unusually large pressure effect on T_c has led to suggestions^{8,12} that the high-temperature superconductivity in the La-Ba-Cu-O and La-Sr-Cu-O systems may be associated with interfacial effects arising from mixed phases; interfaces between the metal and insulator layers, or concentration fluctuations within the K_2NiF_4 phase; strong superconducting interactions due to the mixed valence states; or yet a unidentified phase. Furthermore, we found that when the superconducting transition width is reduced by making the compounds closer to the pure K_2NiF_4 phase, the onset T_c is also reduced while the main transition near 37 K remains unchanged. Extremely unstable phases displaying signals indicative of superconductivity in compounds consisting of phases in addition to or other than the K_2NiF_4 phase have been observed by us,^{8,14} up to 148 K, but only in four samples, and in China,¹⁵ at 70 K, in one sample. Therefore, we decided to investigate the multiple-phase Y-Ba-Cu-O compounds instead of the pure K_2NiF_4 phase, through simultaneous variation of the lattice parameters and mixed valence ratio of Cu ions by chemical means at ambient pressure.

The compounds investigated were prepared with nominal compositions represented by $(Y_{1-x}Ba_x)_2CuO_{4-\delta}$ with $x=0.4$ through solid-state reaction of appropriate amounts of Y_2O_3 , $BaCO_3$, and CuO in a fashion similar to that previously described.⁸ Bar samples of dimensions $1 \times 0.5 \times 4 \text{ mm}^3$ were cut from the sintered cylinders. A four-lead technique was employed for the resistance (R) measurements and an ac inductance bridge for the mag-

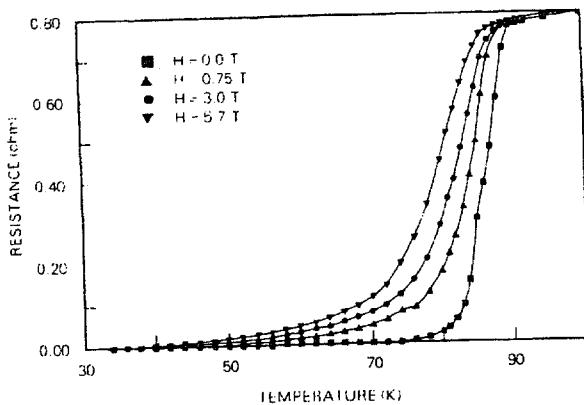


FIG. 1. Temperature dependence of resistance determined in a simple liquid-nitrogen Dewar.

netic susceptibility (χ) determinations. The temperature was measured by means of Au+0.07% Fe-Chromel and Chromel-Alumel thermocouples in the absence of a magnetic field, and a carbon-glass thermometer in the presence of a field. The latter was calibrated against the former without a field. Magnetic fields up to 6 T were generated by a superconducting magnet.

The temperature dependence of R determined in a simple liquid-nitrogen Dewar is shown in Fig. 1. R initially drops almost linearly with temperature T . A deviation of R from this T dependence is evident at 93 K and a sharp drop starts at 92 K. A "zero- R " state is achieved at 80 K. The variation of χ with T is shown in Fig. 2. It is evident that a diamagnetic shift starts at 91 K and the size of the shift increases rapidly with further cooling. At 4.2 K, the diamagnetic signal corresponds to 24% of the superconducting signal of a Pb sample with similar dimensions. In a magnetic field, the R drop is shifted toward lower T . At our maximum field of 5.7 T, the "zero- R " state remains at a T as high as 40 K. Pre-

liminary x-ray powder diffraction patterns show the existence of multiple phases uncharacteristic of the K_2NiF_4 structure in the samples. Detailed analyses are underway.

The above results demonstrate unambiguously that superconductivity occurs in the Y-Ba-Cu-O system with a transition between 80 and 93 K. We have determined the upper critical field $H_{c2}(T)$ resistively. If the positive curvature at very low fields is neglected, one gets a value of dH_{c2}/dT near T_c of 3 T/K or 1.3 T/K, depending on whether $H_{c2}(T_c)$ is taken at the 10% or the 50% drop from the normal-state R . In the weak-coupling limit, $H_{c2}(0)$ is thus estimated to be between 80 and 180 T in the Y-Ba-Cu-O system investigated. We believe that the value of $H_{c2}(0)$ can be further enhanced as the material is improved. The paramagnetic limiting field at 0 K for a sample with a $T_c \sim 90$ K is 165 T. Because of the porous and multiphase characteristics of the samples, it is therefore difficult to extract any reliable information about the density of states from the slope of $H_{c2}(T)$ at T_c on the basis of the dirty-limit approximation.

On the basis of the existing data, it appears that the high-temperature superconductivity above 77 K reported here occurs only in compound systems consisting of a phase or phases in addition to or other than the K_2NiF_4 phase. While it is tempting to attribute the superconductivity to possible nonconventional superconducting mechanisms as mentioned earlier, all present suggestions are considered to be tentative at best, especially in the absence of detailed structural information about the phases in the Y-Ba-Cu-O samples. However, we would like to point out here that the lattice parameters, the valence ratio, and the sample treatments all play a crucial role in achieving superconductivity above 77 K. The role of the different phases present in superconductivity is yet to be determined.

The work at the University of Alabama at Huntsville is supported by NASA Grants No. NAG8-032 and No.

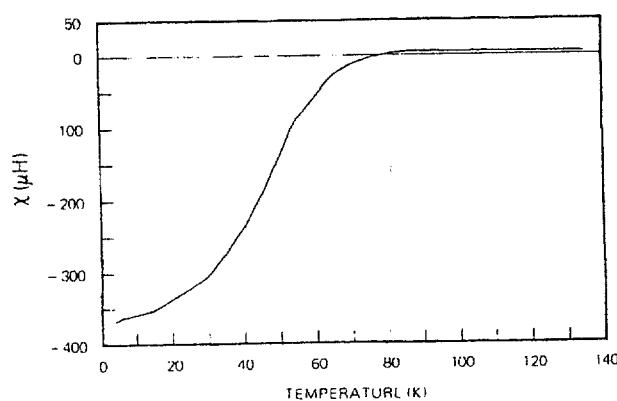


FIG. 2. Temperature dependence of magnetic susceptibility.

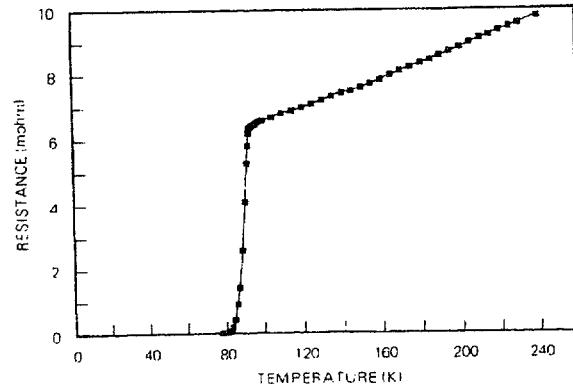


FIG. 3. Magnetic field effect on resistance.

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High-Pressure Study of the New Y-Ba-Cu-O Superconducting Compound System

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The pressure effect on the superconducting state above 77 K in the new Y-Ba-Cu-O compound system has been determined. In strong contrast to what is observed in the La-Ba-Cu-O and La-Sr-Cu-O systems, pressure has only a slight effect on the superconducting transition temperature.

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Recently, Bednorz and Müller reported¹ the possible existence of superconductivity up to 35 K in the La-Ba-Cu-O compound system. The significance of the K_2NiF_4 phase present in their samples was also pointed out. Subsequent magnetic measurements,²⁻⁴ indeed, confirmed the report, and the observed superconductivity was attributed⁵ to the K_2NiF_4 phase. Pressure^{4,6} was found to enhance the superconducting transition temperature T_c of La-Ba-Cu-O at a rate of greater than 10^{-3} K bar⁻¹ and to raise⁷ the onset T_c to 57 K, reaching a "zero-resistance" state at 40 K, the highest in any known superconductor until now. Replacement^{4,8,9} of Ba ions by smaller Sr ions in La-Ba-Cu-O compounds of the K_2NiF_4 structure was also found to enhance the T_c and sharpen the transition. A transition width⁸ of 2 K and an onset⁹ T_c of 48.6 K were obtained at ambient pressure. On the other hand, we found that when the superconducting transition width is reduced by making the compound with a purer and more homogeneous K_2NiF_4 phase, the onset T_c is usually reduced while leaving the main transition at ~ 37 K unchanged. Furthermore, extremely unstable and difficult-to-reproduce phases exhibiting electrical and magnetic signals indicative of superconductivity up to 148 K at ambient pressure have been observed by us^{4,10} in only four samples consisting of more than one phase and often not including the K_2NiF_4 or the ABO_3 perovskite as the major phase. Workers in China¹¹ also reported observing signs of superconductivity in one of the mixed-phase samples at 70 K. This led us to the proposition¹² that T_c above 77 K may exist in compound systems represented generically by the formula $(L_{1-x}M_x)_aA_bD_y$, and not necessarily the pure K_2NiF_4 phase. As shown in the preceding paper,¹³ superconductivity above 77 K is achieved at ambient pressure when $L=Y$, $M=Ba$, $A=Cu$, and $D=O$ with nominal compositions $a=2$, $b=1$, $x=0.4$, and $y=4-\delta$, where δ is undetermined.

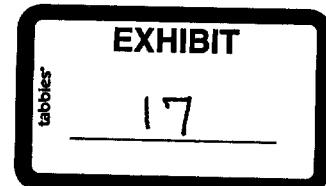
In an attempt to probe the nature of the superconductivity observed, we have determined the hydrostatic effects on T_c of the Y-Ba-Cu-O compound system, resis-

tively, up to 19 kbar. T_c of Y-Ba-Cu-O was affected only slightly by pressure in strong contrast to what is observed for the K_2NiF_4 phase in La-Ba-Cu-O and La-Sr-Cu-O. This, together with our preliminary x-ray powder diffraction data, suggests that the Y-Ba-Cu-O compound system displaying superconductivity above 77 K may be very different from the superconducting La-Ba-Cu-O and La-Sr-Cu-O systems which have only a maximum onset⁹ of 48.6 K at ambient pressure.

The compounds examined were the same as those described in the preceding paper.¹³ They were prepared with nominal compositions represented by $(Y_{1-x}Ba_x)_2CuO_{4-\delta}$ with $x=0.4$ through solid-state reaction of appropriate amounts of Y_2O_3 , $BaCO_3$, and CuO in a fashion similar to that previously reported.⁴ The powder x-ray measurements were carried out with a GE diffractometer with a resolution of $\sim 5\%$. Bar samples of dimensions $1 \times 0.5 \times 4$ mm³ were cut from the sintered cylinders. A standard four-lead technique was used for the resistance (R) measurements. The pressure environment was provided by a Be-Cu clamp with a fluid medium. The pressure was determined by a pressure gauge at room temperature. It is then corrected by subtraction of the loss due to the freezing of the pressure medium at lower temperature, i.e., < 180 K, estimated to be about 2 kbar. The temperature was measured by a Chromel-Alumel thermocouple situated next to the sample.

The Y-Ba-Cu-O compounds with superconductivity above 77 K clearly exhibit more than one phase when examined under an optical microscope, one dark green and the other black. No effort can be made to fit satisfactorily the diffraction patterns with the known K_2NiF_4 layered or ABO_3 perovskite phase. It is therefore evident that the Y-Ba-Cu-O compound exhibiting superconductivity above 77 K may not be identified with the well-known cubic perovskite or the tetragonal layered-structure phase at our present resolution. Detailed analyses are under way.

Typical temperature dependence of R normalized to that at 100 K for simplicity is shown in Fig. 1 at a few



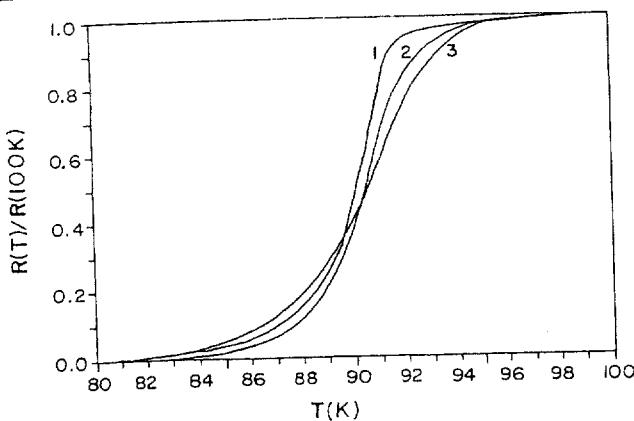


FIG. 1. The temperature dependence of resistance at different pressures: 1 = 0 kbar, 2 = 8.4 kbar, and 3 = 19 kbar.

pressures. At ambient pressure, R initially decreases with temperature linearly and starts to deviate from this linear dependence at ~ 93 K. A "zero- R " state is reached at 80 K. One may define the superconducting onset temperature T_{c0} and the complete temperature T_{cf} as the intersection temperatures of the main part of the transition with the linear extrapolation of the $R(T)$ curve and the "zero- R " line, above and below the transition, respectively. Under pressure, T_{c0} is shifted up slightly and T_{cf} first up and then down, as shown in Fig. 2. The observation is reversible during pressure cycling when proper precautions are taken. The midpoint of the transition, i.e., where $R(T)/R(100\text{ K})=0.5$, changes only slightly. This is in strong contrast to that observed^{4,6,7} previously in the K_2NiF_4 phase of the La-Ba-Cu-O and La-Sr-Cu-O systems with a maximum $T_{c0}\sim 48.6$ K at ambient pressure. The pressure effects on these latter systems are represented by a dashed line also shown in Fig. 2 for comparison.

In conclusion, we have found that pressure has little effect on the superconducting state of Y-Ba-Cu-O, in strong contrast to the behavior of the K_2NiF_4 -phase La-Ba-Cu-O and La-Sr-Cu-O systems. This may be due to chemical pressure associated with the smaller Y atoms already present in Y-Ba-Cu-O. Preliminary x-ray powder-diffraction results indicate that the high-temperature superconductivity in Y-Ba-Cu-O can only be attributed to one or more phases with structures different from the cubic perovskite or tetragonal layered one. The detailed structures of Y-Ba-Cu-O displaying superconductivity above 77 K are being determined. We believe that the transition can be further sharpened by adjustment of the various physical and chemical parameters.

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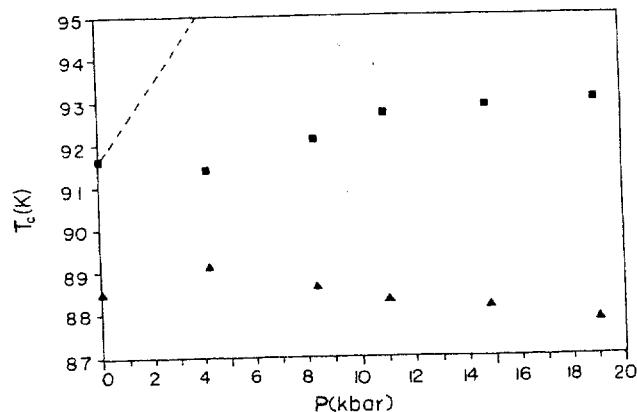


FIG. 2. The pressure effect on the superconducting transition onset temperature T_{c0} (squares) and the complete temperature T_{cf} (triangles) (see text for definition). The slope of the dashed line is for the K_2NiF_4 phase of La-Ba-Cu-O and La-Sr-Cu-O compounds.

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